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(54) Microlatexes

(57) A stable and transparent microlatex is manufactured by first preparing a stable and transparent co-surfactant-free microemulsion of the water-in-oil type by admixing an aqueous solution of a water-soluble vinyl monomer with a hydrocarbon oil and a surfactant, the proportions of the constituents being so selected as to constitute a microemulsion (in particular, the surfactant content of the oil phase is at least 11% by weight), then subjecting the resultant mixture to polymerization and finally recovering the desired microlatex. The microlatex produced can be used in enhanced oil recovery.

GB 2 118 200 A

SPECIFICATION
Microlatexes, their production in oil phase by polymerisation of a water-soluble monomer in a water-in-oil microemulsion, and their use for enhanced oil recovery

This invention concerns the manufacture of stable transparent microlatexes by polymerization of
5 at least one water-soluble vinyl monomer and the use of such latexes in enhanced oil recovery.
In accordance with the present invention, microlatexes are obtained by
(a) preparing a stable and transparent co-surfactant-free microemulsion of the water-in-oil type by admixing (i) an aqueous phase comprising an aqueous solution of at least one water-soluble vinyl monomer with (ii) an oil phase comprising a hydrocarbon oil and at least one surfactant, the
10 proportions of the above constituents being so selected as to satisfy the following conditions, viz:— the surfactant content of the oil phase is at least 11% by weight, the microemulsion is composed of 1—50% by weight of aqueous phase and 99—50% by weight of oil phase, the aqueous phase is composed of 5—55% by weight of the water-soluble vinyl monomer and 95—45% by weight of water, and the mixture of the two phases constitutes a stable and transparent microemulsion;
15 (b) subjecting the microemulsion obtained in step (a) to polymerization conditions, and
(c) recovering the resultant stable and transparent microlatex of high molecular weight.
In carrying out the process of the invention, a water-soluble vinyl monomer or a mixture of vinyl monomers is dissolved in water and dispersed in a mixture of surfactant and oil, the proportions of the constituents corresponding to the monophasic domains, also called microemulsions, of the
20 surfactant/oil/aqueous monomer solution phase gram. The monomer is entrapped in the water-swollen micelles whose average radius is about 4 nanometers. These systems are optically transparent and thermodynamically stable and are thus adapted to photochemical reactions.
The water-soluble monomer, particularly acrylamide, acrylic acid or N-vinyl pyrrolidone, is polymerized photochemically or thermally in microemulsion. The method consists of initiating the
25 polymerization photochemically, for example by ultra-violet irradiation, or thermally with a hydrophobic initiator, for example azobisisobutyronitrile, or a hydrophilic initiator, for example potassium persulphate.
The polymerization takes place very quickly, for example, in a few minutes by the photochemical method: it is quantitative and leads to the formation of a microlatex whose particle radius is of about
30 15 nm with a narrow size distribution range. The systems remain transparent during the polymerization. Their viscosities are low, for example, of a few centipoises (1 centipoise=1 mPa.s).
A major feature lies in the fact that the continuous phase consists of a practically pure hydrocarbon phase. This results from the selection of a surfactant that allows the formation of microemulsions without any added co-surfactant (alcohol or amine). The presence of an alcohol is
35 liable to favour transfer reactions and difficulties of dilution may appear which are attributable to the mixture of solvents constituting the continuous phase. In the above polymerization process, the latexes can be diluted without difficulty to the desired concentration.
The molecular weights of the resultant polymers may reach a few millions, thus showing the absence of transfer reactions. This order of magnitude and the low size of the particles suggest that the
40 number of polymer molecules in a particle is very low, possibly as low as 1. The conformation of macromolecules of large size entrapped in such a reduced space presents interesting and original properties.
The same method, when applied, for example, to the radical copolymerization of acrylamide with methylene-bis-acrylamide, leads to the formation of low-size microgels (about 30 nm in diameter)
45 dispersed in an oily phase. Acrylamide can also be copolymerized with a salt, for example a sodium salt, of acrylic acid.
An alkaline reactant can be used, for example sodium or potassium hydroxide or carbonate. There is thus obtained, by correctly selecting the proportion of alkaline agent, a partially hydrolysed polymer, for example a partially hydrolysed polyacrylamide, which is particularly advantageous for enhanced oil
50 recovery. Another technique consists, however, of effecting the hydrolysis after polymerization. The hydrolysis rate is, for example, 1 to 67%.
The present method is thus distinguished from emulsion polymerization, which leads to latexes of large size. The difference between emulsions and micro-emulsions is as follows, percentages and parts being by weight.
55 Emulsion: a diphasic, turbid, unstable medium. When stirred, particles appear which are dispersed in the water or the oil, depending on the case, and have a wide size distribution range with an average size of the order of 1 micrometer. When polymerized in emulsion, the monomer appears dispersed in the big droplets of the emulsion (diameter 1 to 10 μm) as well as in the small micelles of the emulsifier (diameter 5 to 10 nm).
60 Microemulsion: a swollen, transparent and thermodynamically stable micellar solution which does not need stirring. The droplets are far smaller than in the case of an emulsion, of about 10 nanometers, justifying the name of microemulsion. They also have a narrow size distribution range with an average size of 10 nm. Before polymerization, the monomer is dispersed in the water-swollen micelles of the same size.

To form microemulsions, the surfactant proportion must be fairly high, otherwise only simple emulsions are formed. A concentration higher than 11%, with respect to the hydrocarbon phase, is thus desirable, for example 15 to 40% of this phase.

There is used, for example, 5 to 55% of monomer with 95 to 45% of water. The monomer-containing aqueous phase amounts for example, to 1 to 50 parts, the hydrocarbon phase proportion being 99 to 50 parts.

A preferred class of surfactants is the anionic class of the aerosols OT, such as sodium di-2-ethyl-hexyl sulphosuccinate; other surfactants can be used, provided they are of the water-in-oil type, for example a cationic surfactant such as hexadecylbenzenedimethyl ammonium bromide.

The operation is conducted at, for example, 40—70°C when using a free radical generator. The proportion of the latter is, for example, 0.002 to 0.2 weight %.

The size of the particles dispersed in the initial microemulsion and in the final microlatex has been determined by means of quasi-elastic light diffusion. The light source of the light diffusion apparatus consists of an argon-ion Spectra Physics laser operating at 488 nm. The time correlation function of the diffused intensity is obtained with a digital 72-channel correlator. The correlation data of the intensity have been processed by us of the cumulating method which supplies the average decreasing time $<\Gamma^{-1}>$ of the correlation function and the variance V. The latter measures the amplitude of the decreasing time distribution; it is given by:

$$V=(<\Gamma>^2-<\Gamma^2>)/<\Gamma>^2$$

where $<\Gamma^2>$ is the second moment of the distribution.

For solutions of low polydispersity polymers, the variance is related in first approximation to the polydispersity number Mw/Mn (molecular weight b.w./molecular weight by number) by the relation:

$$Mw/Mn=1+.4V$$

The molecular weight of the resultant polyacrylamide has been measured both by light diffusion and by viscosimetry, using in the latter case the following relationship applicable to aqueous solutions:

$$[\eta]=9.33\times10^{-3} <M>_w{}^{0.75} \ cm^3/g$$

The initial microemulsions remain transparent and stable in the course of the polymerization reaction.

The transparency may be determined by turbidimetry (see, for example, Colloid and Polymer Sciences, Vol. 258 (1980) page 1254). It can be used to characterize the microlatexes obtained according to the invention; this detection method of a transition between a homogeneous macroscopic phase and an emulsion consists of measuring the optical transmission of the sample. As a rule, the percentage of light transmission by turbidimetry is higher than 50% in the case of the microlatexes of the invention, and is higher than 80% and more usually higher than 90% for the starting microemulsions, whereas it is lower than 10% and more usually 0% in the case of the emulsions produced according to prior techniques.

Polymerizations have been conducted in microemulsion with variable acrylamide: water ratios up to 1.3:1. In no case, has phase separation been observed.

The polymerization is fast and a total conversion to polymer is obtained in less than 30 minutes, as confirmed by weighing the polymer and carrying out nuclear magnetic resonance experiments.

Conversely to the high viscosities of the conventional inverted emulsions, the viscosity of the systems is low, about 7—8 centipoises (mPa.s) and is not substantially affected by ultra-violet irradiation. Hence it has been concluded that the polymerization effectively takes place within the micelles.

The microlatexes of the invention can be used to improve enhanced oil recovery, either as such or after partial hydrolysis, in the already known manner described for partially hydrolysed polyacrylamides. They have advantages with respect to the latter, as a result of the lower size of their particles, their lower degree of polydispersity and their thermodynamic stability. They result in a better scavenging of the oil formations and thus in a more efficient oil recovery.

The methods of use of the microlatexes of the invention, as concerns enhanced recovery, do not differ substantially from those described for microemulsions of the water in oil type (see, for example, U.S. Patents Nos. 3,254,714 and 3,467,188) or for similar microemulsions comprising a polysaccharide (see, for example, U.S. Patent No. 3,719,606). These methods can thus be used. The tests effected in the laboratory have shown the efficiency of the microlatexes of the invention.

For enhanced oil recovery, the microlatexes are used after dilution in water, for example field water, at a concentration of, for example, 50 to 5000 ppm by weight of polymer with respect to the aqueous phase.

Enhanced oil recovery is achieved by injecting an aqueous polymer solution into the field through

at least one injection well, circulating it through the formation and collecting the displaced
hydrocarbons through at least one production well.

Other uses are in formation consolidation, in the manufacture of drilling muds, in inhibition of
water inflow when drilling, and as completion or fracturing fluid.

5   In addition to these uses, the water-soluble polymers prepared by microemulsion polymerization
have other uses.

They can serve as coagulants to separate solids suspended in a liquid. The polymer, more finely
dispersed than when obtained by conventional emulsion polymerization, has a higher activity on muds
from sources such as steelworks rolling-mills, coal and potash.

10   Alternatively, they can act as flotation and draining adjuvants in the manufacture of paper: the
addition of the polymer in stable microemulsion improves water draining from the paper sheets.

They can also be used as flocculants for many substrates, such as cellulose fibres and in water
treatment. The water-in-oil microemulsions are converted by addition of water to oil-in-water
microemulsions, where the polymer quickly dissolves into water. The efficiency of the usual polymers is
15   however altered by rapid temperature changes, especially in winter, which favour the aggregation of
the fine polymer particles, thus strongly decreasing their flocculation effect. The polyacrylamides
prepared by the present process of microemulsion polymerization, consisting of low size (50 nm) and
low polydispersity particles, have better properties in this respect.

Finally, the microlatexes can also be used for assembling glass fibres, since they have a low
20   viscosity and a good stability, as well as in the leather industry (finishing), and in paints.

The following Examples illustrate but do not limit the process of the present invention, as well as
showing properties and uses of some of the products obtained.

Example 1

3.5 g of acrylamide is dissolved in 10.4 g of water and the resultant solution is dispersed by
25   stirring into a previously prepared mixture of 68.9 g of toluene, 17.2 g of sodium bis-2-ethylhexyl
sulphosuccinate and 5×10^{-3} g of azobisisobutyronitrile.

After degassing with nitrogen, the resultant transparent system is exposed to ultra-violet
irradiation for about 30 minutes (5 mn is usually sufficient). Stirring is not necessary, since the
microemulsion is stable.

30   The resultant microlatex has a particle radius of about 160 Angstroms (16 nm), whereas the
radius of the droplets of the initial microemulsion was about 38 Angstroms (3.8 nm). This monophasic
microlatex is stable and transparent. The polydispersity number of the polymerized system is low, the
variance being about 0.05 (the variance of the unpolymerized system was about 0.02).

The following Table shows the evolution of the light transmission (%T), determined by
35   turbidimetry, and the evolution of the microlatex viscosity (η in centipoises or mPa.s) during the
polymerization:

Before polymerization		After polymerization	
%T	η cps	%T	η cps
95	3.1	70	1.5

40   The resultant polymer was precipitated by an excess of acetone to characterize it. The molecular
weight, determined by viscosimetry or by light diffusion, is about 3×10^{6}.

Example 2

2.9 g of acrylamide is dissolved in 10.8 g of water and the solution is dispersed in a mixture of
43.6 g of toluene, 42.7 g sodium bis-2-ethylhexyl sulphosuccinate and 0.29 g of azobisisobutyronitrile.
45   The transparent and stable system is degassed and maintained at 60°C for 10 minutes. The percentage
of transmission by turbidimetry decreases from 96% for the initial microemulsion to 55% for the final
microlatex, which is stable and transparent.

The molecular weight of the resultant polyacrylamide, determined by viscosimetry, is 8×10^{5}.

Example 3

50   3.58 g of acrylamide is dissolved in 3.37 g of water; the solution is dispersed by stirring into a
previously prepared mixture of 59.36 g of n-heptane, 33.69 g of sodium bis-ethyl-hexyl
sulphosuccinate and 3.5×10^{-3} g of phenyl dimethoxymethylphenylketone (IRGACURE 651 of Ciba
Geigy). The stable and transparent mixture is irradiated with ultra-violet light at 20°C. The conversion
to polyacrylamide is quantitative and the particle radius of the resultant transparent microlatex is about
55   10 nm, whereas the radius of the droplets of the initial microemulsion was about 7 nm. The % of
transmission by turbidimetry is 96% for the initial microemulsion and 63% for the final microlatex
which is stable and transparent.

Example 4

6.87 g of acrylamide is dissolved into 7.65 g of water; the solution is dispersed by stirring into a mixture of 68.43 g of toluene, 17.04 g of sodium bis-ethyl-hexyl sulphosuccinate and 6.5×10^{-4} g of azobisisobutyronitrile. The transparent and stable mixture is heated to 45°C; after 20 minutes, the conversion to polymer is higher than 97% and the molecular weight of the resultant polymer is 6.3×10^6.

The evolution of the particle size, the viscosity and the transparency of the microlatex is as follows:

Before polymerization			After polymerization		
Particle radius (Å)	T (%)	η (cps)	Particle radius (Å)	T (%)	η (cps)
60	94	5.5	230	70	1.6

Example 5

7.16 g of acrylamide is dissolved into 7.15 g of water and this solution is dispersed in a mixture of 68.53 g of toluene, 17.16 g of sodium bis-ethyl-hexyl sulphosuccinate and 0.71 g of azobisisobutyronitrile. The transparent and stable system is degassed and maintained at 60°C for 10 minutes. A stable and transparent microlatex is obtained.

The molecular weight of the resultant polyacrylamide is 5×10^6.
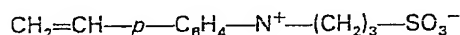
Example 6

4.76 g of acrylamide is dissolved in 4.70 g of water and the solution is dispersed in a mixture of 166.72 g of toluene, 15.86 g of butanol, 7.92 g of sodium dodecylsulphate and 0.03 g of benzoine ethyl ether $C_6H_5CH(OC_2H_5)COC_6H_5$. The transparent system is degassed, but in a nitrogen atmosphere and irradiated with ultra-violet light at 20°C for 12 minutes. The conversion to polyacrylamide is quantitative and the transparency and the viscosity of the microlatex do not change substantially during the polymerization.

Example 7

7.8 g of vinylpyrrolidone is dissolved in 7.8 g of water and the solution is dispersed into a mixture of 70.37 g of n-heptane, 17.89 g of sodium bis-ethyl-hexyl sulphosuccinate and 0.06 g of benzoine ethyl ether $C_6H_5CH(OC_2H_5)COC_6H_5$. The resultant transparent mixture is irradiated with ultra-violet light. The conversion to transparent polyvinylpyrrolidone microlatex is 90%.

Example 8

4.49 g of (3-sulfopropyl)-2-vinylpyridinium betaine

$$CH_2{=}CH{-}p{-}C_6H_4{-}N^+{-}(CH_2)_3{-}SO_3^-$$

is dissolved in 5.36 g of water and the solution is dispersed in a mixture of 71.82 g of toluene, 18.24 g of sodium bis-ethyl-hexyl sulphosuccinate and 0.05 g of potassium persulphate $K_2S_2O_8$. The solution remains transparent and fluid when heated at 50°C for 16 hours. A transparent microlatex of high molecular weight is obtained. The polymer is isolated as a very fine powder by precipitation of the mixture in an excess of methanol.

Example 9

42 g of a 50 weight % solution of acrylamide in water is added to 51.6 g of sodium dioctyl sulphosuccinate dissolved in 206 g of toluene. The inverse transparent microemulsion thus obtained is degassed and irradiated with an UV lamp for 15 minutes. A transparent microlatex is obtained by precipitation of a portion of the resultant microlatex in acetone, successive washings with acetone and methanol and drying up to constant weight. A polyacrylamide having a molecular weight of 10.3×10^6 (by viscosimetry) is obtained with a conversion of 95%.

Another portion of the microlatex (150 g) is admixed with 2.49 g of potassium hydroxide as a solution in 11.4 g of water. The reaction mixture is heated for 2 hours at 65°C and then for 2 hours at 90°C. The polymer obtained after washing with acetone and methanol and drying has a hydrolysis degree of about 30%, as determined by potentiometric determination. The intrinsic viscosity (η) of this copolymer dissolved in water containing 0.1 M of Na Cl is 4,800 cm³/g, as determined with a LS 30 viscosimeter of the Contraves Company and extrapolation at zero concentration and gradient. A solution of this copolymer (concentration: 1000 ppm by weight) is then prepared by dispersing the microlatex into water from a field containing about 30 g/l of dissolved salts, including 8.6 g/l of Na⁺ ions, 1.3 g/l of CA⁺⁺ ions and 0.3 g/l of Mg⁺⁺ ions. This solution is then subjected to a conventional filtration test, as follows:

[1] the solution is passed through a series of 8 μm Millipore filters of a pore radius r_p adapted to the permeability of the rock samples from the field to be treated

$$r_p = \sqrt{\frac{8k}{\varphi}}$$

where k is the permeability and φ the porosity). The injection is effected at a constant rate of $V_{inj.}=0.25$ metre per day with a double-acting pump and at a temperature of 45°C. The pressure drop in mm Hg is measured at the ends of the filter carrier, which contains three 8 μm Millipore filters in series and the results are expressed as the mobility reduction R_λ. The latter is defined as the ratio of the pressure drop measured when passing the polymer solution to the pressure drop measured with the field water.

[2] the relative viscosities of the polymer solution are measured before and after passage through the filters.

[3] the polymer solution is circulated through the same filters at different velocities and the curve $R_\lambda = f(V_{inj.})$ is determined.

[4] field water is circulated behind the polymer solution at different circulation velocities and the curve $R_k = f(V_{inj.})$ is determined, R_k being the permeability reduction observed with the field water.

Table 1 summarizes the results obtained, showing the good quality of the polymer solution and particularly the absence of plugging.

Table 1
Test of filtrability through 8 μm millipore filters in series.

Circulation rate in m/day	R_λ	R_k	η rel
0.5	4.7	1.35	4.70
1	4.7	1.35	4.68
2	4.7	1.47	4.62
5	5.85	1.82	4.35
10	8.1	2.15	4.05

It is also found that the relative viscosity of the polymer solution before and after passage through the filters remains unchanged (η rel=3.13), which confirms the absence of any filter plugging.

The same microlatex is used to prepare a solution in the same field water (30 g/l of dissolved salts) containing 2000 ppm of polymer. This solution is then injected into a core from the field (L=10 cm, d=2.5 cm, k=490 mD) (k is the permeability with respect to water, expressed as milli-darcy) at a rate of 0.4 m/day and the pressure drops at the ends of the core are determined as above. The values of R_λ are determined with the polymer solution and those of R_k with water circulated behind the polymer at different circulation rates.

On the other hand, the Contraves LS 30 viscosimeter is used to determine the values of the relative viscosity η rel at different velocity gradients.

The results of Table 2 show the capacity of the microlatex to circulate through the porous medium; particularly, an apparent viscosity in porous medium higher than 10 is obtained, thus allowing the use of this polymer as mobility buffer behind the previously injected surfactant solution. No plugging of the input surface of the core is observed.

Table 2
Filtrability test through a field core

Circulation rate in m/day	R_λ	R_k	η rel LS 30
0.4	13.8	1.5	12.3
0.8	13.9	1.5	11.8
2	13.9	1.55	10.3
4	15.1	1.6	9.3
8	27	1.75	7.8

Inhibition of water inflow into production wells

A porous medium (L=10 cm, cross-section=20 cm²) consisting of the mixture of 84% coarse sand particle size: 200 to 300 μ), 8% calibrated silica (particle size: 15 to 80 μ), 4% montmorillonite and 4% kaolinite and having a water permeability of about 1 darcy is saturated with brine containing 20 g/l of NaCl at 30°C. The acrylamide-acrylate copolymer prepared from the corresponding microlatex and disposed at a rate of 1600 mg/l in water containing 20 g/l of NaCl is injected into this

porous medium. This solution has a viscosity of 7.9 cps. An amount representing about 10 times the pore volume is injected to completely saturate the core and the polymer solution is then displaced with water containing 20 g/l of NaCl up to stabilization of the pressure drops at the ends of the core. The ratio of the water permeabilities after and before injection of the polymer solution is 7.

The same experiment is repeated with an identical porous medium, but with a solution containing 3000 ppm by weight of copolymer; the permeability reduction is 12.3.

These experiments show that the copolymer can be easily injected in a clayish sand of average permeability and can be used to reduce water inflow into production wells.

Example 10

25 g of an aqueous solution containing 2 g potassium carbonate and 7 g of acrylamide is added to 30 g of sodium dioctyl-sulphosuccinate dissolved in 115 g of toluene containing 10 mg of AIBN. The transparent and stable mixture is degassed and irradiated with an UV lamp for 1 hour. The mixture is then heated for 2 hours at 65°C. A transparent microlatex of high molecular weight is obtained. A fraction of the polymer is isolated by precipitation into acetone, washed several times with acetone and methanol and finally dried up to constant weight. The so-obtained polyacrylamide has a hydrolysis rate of about 20%.

Claims

1. A process for manufacturing a stable and transparent microlatex comprising

(a) a stable and transparent, co-surfactant-free microemulsion of the water-in-oil type by admixing (i) an aqueous phase comprising an aqueous solution of at least one water-soluble vinyl monomer with (ii) an oil phase comprising a hydrocarbon oil and at least one surfactant, the proportions of the above constituents being so selected as to satisfy the following two conditions.

(1) the surfactant content of the oil phase is at least 11% by weight, the microemulsion is composed of 1—50% by weight of the aqueous phase and 99—50% by weight of the oil phase and the aqueous phase is composed of 5—55% by weight of the water-soluble vinyl monomer and 95—45% by weight of water, and

(2) the mixture of the two phases constitutes a stable and transparent microemulsion;

(b) subjecting the microemulsion obtained in step (a) to polymerization conditions, and

(c) recovering the resultant stable and transparent microlatex of high molecular weight.

2. A process according to Claim 1, in which the surfactant concentration is from 15 to 40 weight % in the oil phase.

3. A process according to Claim 1 or 2, in which the monomer is acrylamide.

4. A process according to Claim 1 or 2, in which the monomer is acrylic acid.

5. A process according to Claim 1 or 2, in which the monomer is N-vinyl pyrrolidone.

6. A process according to any one of Claims 1 to 5, in which the surfactant is of the anionic type.

7. A process according to any one of Claims 1 to 5, in which the surfactant is sodium di-2-ethylhexylsulphosuccinate.

8. A process according to Claim 1 substantially as hereinbefore described in any appropriate Example.

9. A microlatex obtained by a process according to any one of Claims 1 to 8.

10. An enhanced oil recovery procedure using a microlatex according to Claim 8.